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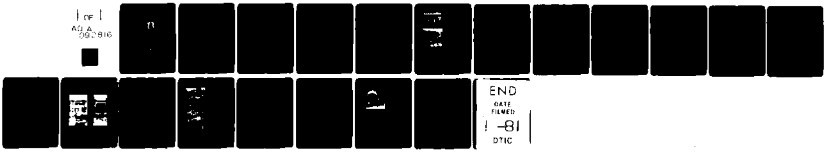

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SILICON AND CIVILIZATION

by

Grzegorz Basinski

FOREIGN TECHNOLOGY DIVISION

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SILICON AND CIVILIZATION by Grzegorz Basinski

Silicon belongs to the most abundant of elements in nature. Its value in the external parts of the Earth's crust is estimated at about 26% gravimetric, which corresponds to about 16% atomic--means that every sixth atom of the external shell of the terrestrial globe is a silicon atom.

We do not meet pure silicon in nature; it appears solely in a combined state chiefly in the form of silicon dioxide (SiO_2), or so-called silicas, and very complex compounds--silicates and aluminosilicates. Silicon dioxide, contained in silica, silicates and aluminosilicates, is the basic component of the lithosphere, i.e., the external crust of the Earth (barring water reservoirs and the atmosphere surrounding the Earth), its quantity approaches 52% of the whole lithosphere.

Silica appears both in a crystalline form, in the form of three main variations--first of all, quartz, and in smaller amounts tridymite and crysto-balite, and in a structureless form as in so-called flint. Quartz is the basic component of many extrusive rocks, such as granite, gneiss, quartzite, sand-stone and others. As the result of the weathering of these rocks and then the rinsing out from them by water, of fine particles of quartz, on the bottom of water reservoirs there opened up wide deposits of sand. Large, well-formed, free of admixtures, colorless quartz crystals appear in the form of so-called mountain crystal. Semi-precious stones such as amethyst, violet colored by admixtures of iron, citrin, golden yellow in color or lemon yellow, also with iron admixtures, or also chrysoprase, colored green by admixtures of nickel are quartz crystals colored due to the presence of admixtures.

Besides flint, minerals such as agate, onyx or jasper also belong to the structureless varieties of silica. Silica can also appear in nature in shapeless form, or so-called amorphous, as strata of diatomaceous earth, or also in the form of the precious stone--opal.

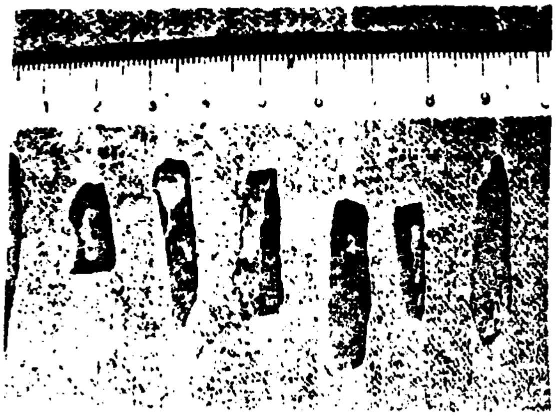
As mentioned, silicon dioxide in large quantities enters into the composition of very complex compounds, silicates and aluminosilicates. Silicates are built of SiO_2 and oxides of metals, chiefly iron-group metals and alkaline metals and earths. Aluminosilicates contain, besides silicon dioxide and metal oxides, aluminum trioxides. Many minerals, which often have a very complex chemical composition, of which the lithosphere is built, belong precisely to these two groups of compounds--silicates and aluminosilicates.

In contrast with the inanimate world, in living organisms silicon is met only sporadically and even then in small quantities. Silica is found in blades of grass and grain, in reed and bamboo shoots, where it serves to stiffen the stalk.

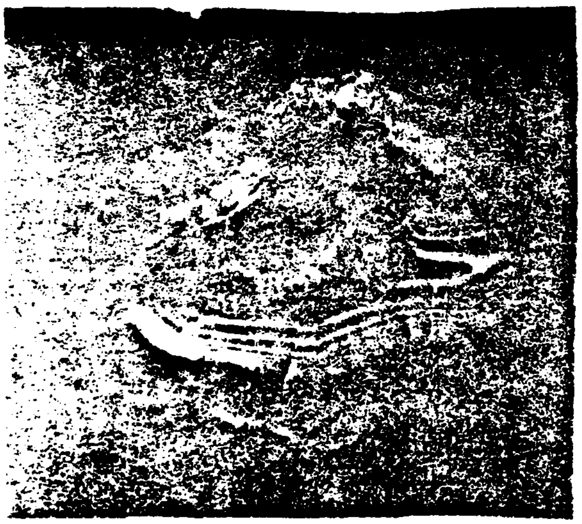
Diatomite skeletons and those of water creatures, which after mortification fall to the bottom of the waters creating strata of diatomaceous earth are also built of silica.

Minerals containing silicon have found wide use in man's life since prehistoric times. The oldest tools--knives, pestles, scrapers--which early man used--were made from pieces of flint peeled off of rock. The oldest flint tools found in eastern Africa in the terrains of Kenya and Ethiopia, come from before 1,750,000 years. From sharpened fragments of flint in a later period arms were also made--arrowheads and hatchet blades, pieces of flint were also used to spark fires. In Poland in the Opatow region of the Kielce province a flint mine from the Neolite period was preserved.

Mountain crystal even in the olden times was used to make jewelry, and in a later period in the Middle Ages and in modern times it was used also to make vessels and other artistic objects. As a point of interest it is worth mentioning that in one of the oldest uncovered settlements of a local type in the region of Anatolia (area of today's Turkey), dating from before 9,000 years, in the underground dwellings of various kinds images were found painted with a dye to which powdered mountain crystal was added. In the light of resinous chips these paintings make an uncanny impression from which we can assume that they at one time served magic purposes.



Early flint tools found in Lascaux cave



Ground agate from Zelenic (Czech.)

Natural size - 12 cm.

In decorative craft precious and semi-precious jewels have been widely used for a long time, such as agate, amethyst, jasper, onyx, opal and many others. Agate, in view of its great hardness, is used in the production of mortar, prisms for analytical balance and other modern elements of laboratory equipment used in chemistry.

Silicon dioxide since the earliest times has found application in glass production. Silica glass, found everywhere in daily life, is gotten by fusing sand with soda (Na_2CO_3) and with limestone ($CaCO_3$) at a temperature of about 1500°C and then forming by blowing, drawing, rolling, etc. Soda-lime glass ($Na_2O \cdot CaO \cdot 6\ SiO_2$) fused in a glass-works serves in the production of window panes. Potassium—lime glass, used in making laboratory vessels, with regard to the increased softening point, is made by mixing sand and lime not with soda, but with potassium (K_2CO_3). The addition of oxides borium (B_2O_3) and aluminum (Al_2O_3) to glass increases its chemical and thermal resistance; Jena glass, from which laboratory equipment is produced, has the following chemical composition: 74.5% SiO_2, 8.5% Al_2O_3, 4.6% B_2O_3, 7.7% Na_2O, 3.9% BaO, 0.8% CaO, 0.1% MgO.

Potassium-lead glass so-called crystal, from which decorative vessels are made, is obtained by fusing sand with potash and litharge (PbO).

Quartz glass made in electric ovens by fusion of quartz sand exclusively has particularly valuable properties desired in technology. Quartz glass is very resistant to temperature change since it has a very small coefficient of thermal expansion, is resistant to the activity of acids except for hydrofluoric acid (HF), and melts only at a temperature higher than 1400°C (usually silicate glasses melt at 600-800°C). The properties mentioned of quartz glass give rise to the fact that it is used everywhere to produce laboratory glass and glass elements of chemical apparatus. Another property of quartz glass is its transmission of ultraviolet rays. For that reason quartz glass is used to make many parts of special optic systems and quartz lamps, being the source of ultraviolet rays.

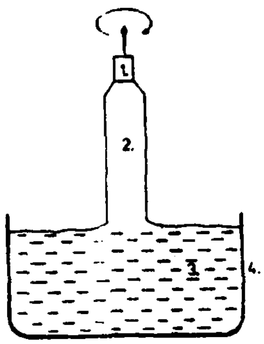
Aluminosilicates, containing silicon dioxide, enter into the composition of various kinds of clays used in the production of ceramic materials such as stoneware, faience, brick, and the like. From a 50% mixture of kaoline, clay containing mainly kaolinite ($Al_2/OH/_4Si_2O_5$), 25% quartz and 25% feldspar, after appropriate formation, firing at 900°C, covering with glaze by immersion in a water suspension of a ceramic mass and another firing at 1400°C, porcelain products are obtained.

Silicon compounds, as the result of great specific surface (ratio of the surface of a specific amount of chemical compound to its mass), can adsorb, or combine on their surface large amounts of liquids or gases from the environment. One of the most commonly used silicon adsorbents is silicagel, built of SiO_2 and chemically bonded ~~bounded~~ with it, water, in a proportion of 1 particle H_2O for 5-10 particles SiO_2, obtained as a result of the condensation of silicon acids from a water solution, and then their drying in the air. Silicagel, appearing in the form of minute grains, is widely used for: absorbing vapor from gases, adsorbing vapors of alcohol, gasoline and other organic compounds, purifying liquids, and also as a catalyst for many chemical reactions. Likewise, diatomaceous earth has a well developed surface and great adsorptive capability, among others it can absorb a triple excess of nitroglycerin in proportion to its own mass, which was used in producing dynamite (an explosive medium composed of 75% nitroglycerine and 25% diatomaceous earth), more shock resistant than nitroglycerin and thus easier to transport.

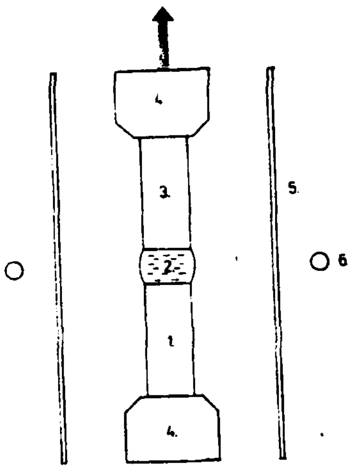
Silicon in the form of a chemical element was obtained for the first time in 1823 by the Swedish scientist Jöns Jacob Berzelius as a result of the reaction of silicon tetrafluoride (SiF_4) with potassium. Presently two main methods are used to obtain silicon: the laboratory method, depending on the reduction of silicon tetrachloride ($SiCl_4$) by soda, and the industrial method, in which silicon dioxide (SiO_2) is reduced by carbon. Crystalline silicon obtained by this method , a dark gray substance resembling graphit in color and finish having a density of 2. 33 g/cm^3, melts at 1423^{o}C (liquid silicon boils at about 2630^{o}C. Crystalline silicon surpasses graphite considerably by its hardness. For graphite is an allotropic variation of carbon crystallizing in a hexagonal arrangement, whose individual planes are free of strong reciprocal bonds , while silicon crystallizes in a regular arrangement, creating a crystal lattice analogous to the crystal lattice of a diamond.

The particular physical and chemical properties of silicon resulted in the fact that in the periodic system it was found in the III period in group IV. An atom of silicon has four valent electrons and with their help it can join by covalent bonds with four other silicon atoms, creating in this way a crystal lattice. Nevertheless a certain small portion of electrons, as a result of the proper amount of energy being delivered to them, loses its place in the chemical bond and becomes free carriers of a charge being able to move around within the compass of the entire crystal. The number of these electrons freed from the bonds, and what follows after that, the electric conductivity of silicon, increases together with an increase in temperature. These electrons give the silicon crystal semiconductive properties, which brings about the fact that silicon is an unusually valuable raw material in the production of various types of semiconductive devices.

Besides silicon in the form of an independent semiconductor, i.e., free of impurities, doped silicon is used in the production of these same devices. As a result of silicon doping by atoms of the elements from group V, so-called donors, e.g., phosphorus or antimony, a type-n semiconductor is obtained, indicating electron conductivity. An atom of donor impurity builds itself into the crystal lattice in the place of silicon, for whereas it has five valent electrons and can create only four bonds with adjacent silicon atoms, because of this fifth electron, not participating in the chemical bonds, it can become liberated



Extraction of silicon monocrystal by Czochralski method: 1-nucleus in holder, 2-drawn crystal, 3-melted silicon, 4-crucible



Extraction of silicon monocrystal not using crucible: 1-polycrystalline silicon, 2-melted silicon, 3-monocrystal, 4-holders, 5-reactor walls, 6-high frequency coil

easily and become a free carrier of the charge, responsible for electron conductivity.

Conversely the situation presents itself in the instance of silicon doping by atoms of acceptors, i. e., elements from group III, e. g., borium or aluminum.

Such an atom has only three valent electrons so that building itself into the silicon lattice it can create bonds only with the three adjacent atoms; it cannot create a fourth bond since an electron is missing in this place, or there exists, a so-called positive hole.

The hole can move from atom to atom and then we have to deal with a so-called hole conductivity, or p-type conduction; the apparent movement of the hole is of course, caused by the actual movement of electrons in the opposite direction. Filling the unoccupied places, they give rise to the appearance of a hole in others. A band model of a solid body more precisely describes the phenomena of independent and admixture conductivity.

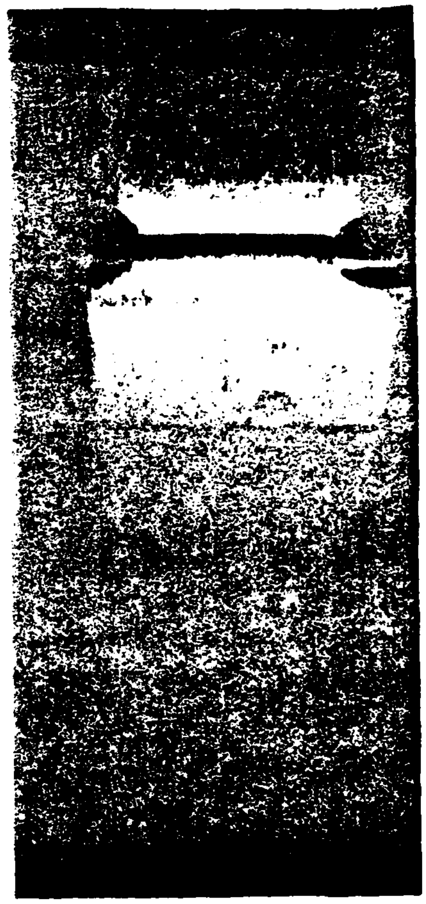
Quartzite, a mineral built chiefly of quartz, is used to produce silicon on an industrial scale. Quartzite undergoes reduction by coke in electric furnaces. As a result of this reaction a product arises containing 96-99% Si. Since impurities in the silicon used to create semiconductive devices cannot exceed 10^{-6}%, the product thus obtained is directed for further processing. After grinding, it is subjected to the action of gaseous hydrogen chloride (HCl), which as a result, yields a mixture of two low boiling liquids, trichlorosilane ($SiHCl_3$) and silicon tetrachloride ($SiCl_4$), with small additives of other compounds. Trichlorasilane separates by distillation from silicon tetrachloride, and then rectifies three times. Such a purified trichlorosilane is reduced by hydrogen at 1300°C in special furnaces with rods placed inside covered with polycrystalline silicon, which increase their diameter in the course of the technological process on account of the settling on it of silicon arising from the reduction of $SiH\ Cl_3$.

The polycrystalline silicon obtained in this way does not lend itself to the production of semiconductive elements, since it establishes the adhesion of fine grains (crystallites) of silicon, which brings about the fact that it does not have, in all its volume, uniform very specific physical-chemical and mechanical properties. To improve its properties it is necessary to obtain from silicon polycrystals uniform monocrystals, free of granular structure. For this purpose silicon undergoes monocrystallization during which the polycrystal heats to a melting point and then very slowly draws out a monocrystal, growing in the nucleus in the course of slow cooling of the melted silicon.

Two monocrystallization methods are used universally:

- the method of Czochralski, a known Polish chemist, based on immersion of monocrystal nucleus in a crucible containing melted silicon and its slow withdrawal with simultaneous constant rotation. As a result of this the liquid silicon, which is drawn together with it, freezes, creating a monocrystalline roll; and

Silicon monocrystal drawn without crucible



Silicon monocrystal drawn by Czochralski method

- non-crucible method, based on immersion of monocrystal nucleus in melted end of polycrystalline roll and then moving the roll through a high temperature zone, obtained as the result of induction heating, so that at every moment only a narrow section of the silicon roll is melted, and after leaving the increased temperature zone, freezes in the form of a monocrystal on the existing nucleus.

To create 1 kg. of silicon monocrystal about 30 kg. of metallurgical silicon must be used. In Poland silicon production was begun in 1965 at the Nitrogen Plant in Tarnow, and the production yield amounts to several tons of silicon yearly.

Monocrystalline silicon serves to make diodes, transistors, silicon controlled rectifiers, self-contained systems, photo-electric cells and photo elements and other semiconductive equipment, used to produce such devices as radio and television receivers, tape recorders, phonographs, mini-calculators and many others.

Besides electronics, silicon found wide application in metallurgy. This is a result of its chemical properties, especially its great resistance to the action of acids. For metallurgical purposes large amounts of an alloy of iron with silicon, so-called ferrosilicon (ferrosilicium), is used, containing 25-90%

The process of monocrystal generation in the reactor can be observed through a sight-glass.

Equipment for producing monocrystals by non-crucible method.

silicon and iron, and moreover fine admixtures of carbon, manganese, phosphorus and sulfur in amounts not exceeding 1%. Such an alloy is obtained as a result of a reduction by carbon of a mixture of sand and iron ore in electric furnaces.

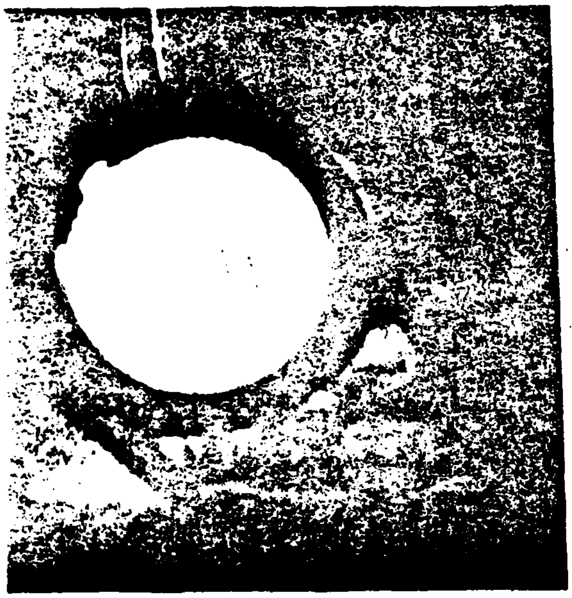
Ferrosilicon is used to reduce steel in the Bessemer process, as well as to produce various types of steel having special properties. Acid resistant steel, so-called duriron, containing about 15% silicon, serves to create apparatus and installations used in the chemical industry. From steel plate, containing several percent silicon and small amounts of carbon, cores for transformers are produced due to the very great value of the magnetic permeability of such steels.

Alloys of silicon with copper, aluminum and manganese are also manufactured and find use in various branches of technology.

If sand is roasted in furnaces at about 2000°C with an excess of coke, then not technological silicon is obtained, only silicon carbide (SiC), or so-called carborundum, a substance with a hardness close to diamond, very resistant to the action of high temperatures and chemical agents. The properties mentioned of carborundum bring about the fact that it is used to manufacture abrasive disks, crucibles, heating elements for electric stoves, etc.

Organic compounds of silicon, so-called silicones, resistant to the action of chemical agents and increased temperature, have found universal application. Having low pressure, a pair of silicone lubricants are used for lubricating microsections of vacuum equipment, glass chemical equipment, electric engine bearings, etc. Silicone resins are used in the production of electrical insulation of equipment operating at high temperatures, as well as in the manufacture of several kinds of varnishes. Silicone rubber has properties resembling regular vulcanized rubber but is more resistant to effects of high temperature. Silicone oils are widely used: they are used as liquid nonconductors, agents in the production of pastes and antiadhesive and antifoam substances, oils for lubricating vacuum pumps, additives to enamels and cosmetics, and even as creams to cure skin ailments.

From the other uses of silicon it is worth noting halogen compounds. Silicofluoric acid (H_2SiF_6), obtained in the hydrolysis of silicon tetrafluoride (SiF_4), as well as its salts, being strong poisons, are used as bactericidal agents, among others, for coating wood for the purpose of preventing rotting. Silicon tetrachloride, ($SiCl_4$) obtained by passing chlorine over a mixture of sand and coke, hydrolyzing,forms of a particle of solid SiO_2 and gaseous hydrochloride, as a result of which it is used in creating smoke screens.



View of the interior (magnified) of reactor for non-crucible extraction of silicon monocrystals. The horizontally placed coil winding can be seen. On the first plan--arm with ready monocrystal.

As can be seen, the use of silicon is a necessary element of the progress of civilization. Silicon, since the remote, prehistoric times, played an important role in the life of human society. Silicon tools and arms helped early man to endure in a world surrounding him with enemies, and then to climb up to a higher level of development. From the silicon compounds contained in aluminums man learned in ancient times to fire vessels and to render glass from sand. In the 19th century when there was a quick development of metallurgy, silicon proved necessary as a component of many kinds of steel, important and necessary in economy. All of contemporary electronics depends on silicon. It can be expected that in the future silicon, and especially its organic compounds--because of their properties, above all the great resistance to the disadvantageous influences of the surrounding environment--will have many new uses, particularly if they will be brought up to a wide scale of action for the purpose of controlling cosmic space.